PREFACE

Materials chemistry basically deals with rational design and synthesis of new solids exhibiting various functional properties. A sound knowledge of crystal structures and chemical bonding is needed to understand the properties of materials. Space group, cell parameters and atomic positions provide a basic crystallographic description of the structure. Crystal structure could be described in a detailed way in terms of close packing of anions and occupancy of cations in different coordination sites. The coordination polyhedra and their interconnectivity bring out the interrelationships between different structures and the properties exhibited.

Transition metals (TMs) are d-block elements which occupy groups 3-12 in Periodic Table. IUPAC defines a TM as 'an element whose atoms have partially filled d-shell, or which can give rise to cations with an incomplete d-shell'. The partially filled d-shell in TMs plays an important role in various chemical and physical properties of TMs. Although TM cations can form compounds with different anions, most of the TM containing compounds are metal oxides due to the large free energies for formation of oxides. Binary TM oxides adopt different kinds of structures among which rock salt (e.g. NiO), rutile (e.g. TiO_2), and corundum (e.g. Cr_2O_3) are most common. Ternary TM oxides are also known to form in variety of structures with the perovskite (e.g. $BaTiO_3$), and the spinel (e.g. $MgFe_2O_4$) structures being well known.

TM oxides exhibit a broad range of electronic and magnetic properties. TM oxides, at one end, display metallic behaviour (e.g. ReO_3, RuO_2, $LaNiO_3$) due to the delocalized electrons and at other end, show insulating behaviour (e.g. NiO) due to the localized electrons. In between, TM oxides have semiconducting properties involving either the hopping of carriers (e.g. partially reduced TiO_2, Nb_2O_5, WO_3 and so on) or the electron excitation from the valence band to the conduction band (e.g. SnO_2). TM oxides are known to have diverse magnetic properties:

diamagnetic (e.g. TiO_2, ZrO_2), paramagnetic (e.g. VO_2, NbO_2), ferromagnetic (e.g. CrO_2, $La_{0.67}Ca_{0.33}MnO_3$), ferrimagnetic (e.g. Fe_3O_4, $MnFe_2O_4$) and antiferromagnetic (e.g. NiO, $LaCrO_3$). TM oxides with partially filled 3d-shell are expected to be 'metallic' according to Bloch-Wilson theory, but in practice they are *Mott insulators* (localized 3d electrons) because of correlation energy (U) involved in the transfer of d-electrons between adjacent sites. Certain TM oxides also show insulator-metal (I-M) transitions induced by change of temperature, pressure or composition. For example, VO_2 and Ba_2IrO_4 are known for their temperature and pressure induced I-M transitions, respectively. $La_{1-x}Sr_xCoO_3$ becomes metal at a particular Sr concentration being one of the examples for composition-dependent I-M transition.

TM oxides are usually synthesized by conventional *ceramic method* in which stoichiometric mixture of starting materials is reacted at elevated temperatures. Multiple prolonged heating with intermittent grindings in ceramic method generally results in thermodynamically controlled products. The *metastable* phases which are of interest may not be obtained by ceramic method. *Chimie douce*/soft chemistry methods are generally adopted to stabilize the *metastable* phases. The guiding principle behind the *chimie douce* is to have kinetic control (rather than thermodynamic control) to realize *metastable* phases. Accordingly, *metastable* derivatives are obtained by choosing appropriate precursors, or adopting sol-gel and molten flux or ion exchange/intercalation methods.

The **present thesis** is devoted to an investigation of transition metal oxides towards development of functional materials exhibiting visible light absorption/emission and lithium insertion/extraction for cathode materials in lithium ion battery. TM oxides find application as photovoltaic materials, luminescent emission materials, photocatalysts, light absorption/pigment materials and so on, based on their optical properties. Ferroelectric TM oxides with perovskite structure [Green coloured $(KNbO_3)_{1-x}(BaNi_{1/2}Nb_{1/2}O_{3-\delta})_x$] are studied currently as photovoltaic materials which show high open circuit voltage (V_{oc} = 3.5 V) despite very low short circuit current (V_{sc} = 40 nA cm^{-2}). TM oxides are also known to

exhibit photoluminescent emission which could be due to the doping activator ions (e.g. Mn^{II} doped Zn_2GeO_4) or TM oxide (e.g. $CaWO_4$) itself being self-activator. While the green and red emissions are common for TM oxides, blue emission is rare (e.g. Ar^+ irradiated $SrTiO_3$ is a blue emitter). Coloured TM oxides with band gap in visible region are employed as photocatalysts for solar water splitting (e.g. yellow $BiVO_4$, yellow Ag_3PO_4, yellow TaON, red Fe_2O_3) and photo-oxidation of organic pollutants (e.g. $TiO_{2-x}N_x$ and $CaCu_3Ti_4O_{12}$). The coloured TM oxides also find application as pigments from early times, for example, Egyptian blue ($CaCuSi_4O_{10}$), Han blue ($BaCuSi_4O_{10}$), Han purple ($BaCuSi_2O_6$), Malachite green ($Cu_2CO_3(OH)_2$), Ochre red (Fe_2O_3) and many others. A list of pigments based on TM oxides is given in Table 1. Pigment materials are applied as colouring materials in inks, dyes, paints, plastics, ceramics glazers, enamels and textiles.

Table 1. List of TM oxide based pigments and their colours

Pigment colour	**Compound**
White	Titanium dioxide (TiO_2)
Black	Iron oxide black (Fe_3O_4)
Red	Iron oxide red (Fe_2O_3), $Ca_{1-x}La_xTaO_{2-x}N_{1+x}$ (yellow-red)
Orange	Iron oxide orange (Fe_2O_3)
Yellow	Yellow ochre [$FeO(OH)\cdot H_2O$]
Green	Malachite green [$Cu_2CO_3(OH)_2$], Viridian ($Cr_2O_3.\ 2H_2O$), Y_2BaCuO_5
Blue	Egyptian blue ($CaCuSi_4O_{10}$),Cobalt aluminate ($CoAl_2O_4$), $YIn_{1-x}Mn_xO_3$
Purple	Han purple ($BaCuSi_2O_6$)
Violet	Cobalt phosphate [$Co_3(PO_4)_2$]

Colours of the TM oxides arise from visible light absorption due to the ligand field d-d electronic transitions. Though d-d transitions are parity forbidden, the selection rules get relaxed due to different reasons such as symmetry reduction (due to distortion) and vibronic couplings. The colour of the TM oxides is influenced mainly by two factors (i) oxidation state of TM ion present and (ii) ligand field around the TM ion produced by anion geometry.

In order to develop new pigment oxides, our strategy was to choose colourless metal oxides having unusual (five coordinated geometry) or irregular/distorted (distorted octahedral/tetrahedral) coordination geometries around metal ion and produce coloured oxides by substituting 3d-TM ions at the metal ion site. We made a detailed study on the origin of the colour and pigment quality of the resulting coloured oxides.

In the present thesis, which has two parts, the first part (**Part 1**) discusses the development of 3d-TM ion substituted coloured oxides with potential for pigment applications.

Chapter 1.1 describes the purple inorganic pigment, $YGa_{1-x}Mn_xO_3$ ($0 < x \leq 0.10$), based on the hexagonal $YGaO_3$. The metastable series of oxides were prepared by a sol-gel technique where the dried gels, obtained from aqueous solutions of metal nitrates-citric acid mixtures, were calcined for a short duration in preheated furnace around 850°C/10 mins. The purple colour of the oxides arises from the specific trigonal bipyramidal ligand field around Mn^{III} that obtains in the $YGaO_3$ host. Other hexagonal $RGaO_3$ hosts for R = Lu, Tm and Ho substituted with Mn^{III} also produce similar purple coloured materials.

In **Chapter 1.2**, we present a study on substitution of 3d-TM ions in $LiMgBO_3$ host [where Mg(II) has a trigonal bipyramidal (TBP) oxygen coordination)]. We find that single-phase materials are formed for $LiMg_{1-x}Co(II)_xBO_3$ ($0 < x \leq 1.0$), $LiMg_{1-x}Ni(II)_xBO_3$ ($0 < x \leq 0.1$), $LiMg_{1-x}Cu(II)_xBO_3$ ($0 < x \leq 0.1$) and also $Li_{1-x}Mg_{1-x}Fe(III)_xBO_3$ ($0 < x \leq 0.1$) of which the Co(II) and Ni(II) derivatives are strongly coloured, purple-blue and beige-red

respectively, thus identifying TBP CoO_5 and NiO_5 as the new chromophores for these colours.

Chapter 1.3 describes the synthesis, crystal structures and optical absorption spectra/colours of 3d-TM substituted α-$LiZnBO_3$ derivatives: α-$LiZn_{1-x}M^{II}_xBO_3$ [M^{II} = Co^{II} ($0 < x < 0.50$), Ni^{II} ($0 < x \leq 0.05$) and Cu^{II} ($0 < x \leq 0.10$)] and α-$Li_{1+x}Zn_{1-2x}M^{III}_xBO_3$ [M^{III} = Mn^{III} ($0 < x \leq 0.10$) and Fe^{III} ($0 < x \leq 0.25$)]. The crystal structure of the host α-$LiZnBO_3$, which is both disordered and distorted with respect to Li and Zn occupancies and coordination geometries, is largely retained in the derivatives, giving rise to unique colours [blue for Co^{II}, magenta for Ni^{II} and violet for Cu^{II}], that could be of significance for the development of new, inexpensive and environmentally-benevolent pigment materials, especially for the blue colour. Accordingly, the work indentifies distorted tetrahedral MO_4 (M = Co, Ni, Cu) (together with a long M-O bond that gives a trigonal bipyramidal geometry) structural units as the new chromophores for the blue, magenta and violet colours respectively, in the α-$LiZnBO_3$ host.

In **Chapter 1.4**, we describe the synthesis, crystal structures and optical absorption spectra of 3d-TM substituted *spiroffite* derivatives, $Zn_{2-x}M_xTe_3O_8$ (M^{II} = Co, Ni, Cu; $0 < x \leq 1.0$). The oxides are readily synthesized by solid state reaction of stoichiometric mixtures of the constituent binaries at 620°C/12h. Rietveld refinement of the crystal structures from powder XRD data shows that the Zn/MO_6 octahedra are strongly distorted, as in the parent $Zn_2Te_3O_8$ structure, consisting of five relatively short Zn/M^{II} – O bonds (1.898 – 2.236 Å) and one longer Zn/M^{II} – O bond (2.356 – 2.519 Å). We have interpreted the unique colors and the optical absorption/diffuse reflectance spectra of $Zn_{2-x}M_xTe_3O_8$ in the visible, in terms of the observed/irregular coordination geometry of the Zn/M^{II} – O chromophores. We could not however prepare the fully-substituted $M_2Te_3O_8$ (M^{II} = Co, Ni, Cu) by the direct solid state reaction method. Density Functional Theory (DFT) modeling of the electronic structure of both the parent and the transition metal substituted derivatives provides new insights into the bonding and the role of transition metals toward the origin of color in these materials. We believe

that transition metal substituted spiroffites $Zn_{2-x}M_xTe_3O_8$ reported here suggest new directions for the development of colored inorganic materials/pigments featuring irregular/distorted oxygen coordination polyhedra around transition metal ions.

Red coloured materials are rare in nature. Li_2MnO_3 is a unique oxide with an unusual red colour imparted by Mn^{IV} ions. **Chapter 1.5** describes a detailed experimental investigation of Li_2MnO_3 together with other related Mn^{IV} oxides that probes the red colour of Li_2MnO_3 as well as its photoluminescence. Optical absorption spectra reveal a strong band gap absorption with a sharp edge at ~ 610 nm and a transparent region between ~ 610 and ~ 650 nm that causes the red colour of Li_2MnO_3 samples. Octahedral Mn^{IV} ligand field transitions, corresponding to both Mn^{IV} at ideal sites and Mn^{IV} displaced to Li sites in the rock salt based layered structure of Li_2MnO_3, are observed in the excitation spectra of Li_2MnO_3 samples. Optical excitation at the ligand field transition energies produces tunable emission in the red-yellow-green region, rendering Li_2MnO_3 a unique Mn^{IV} oxide. The honeycomb ordered [$LiMn_6$] units in the structure likely causes both the absorption and photoluminescence properties of Li_2MnO_3.

Lithium containing TM oxides with rock salt related structure are being investigated extensively for application as next generation cathode materials for Lithium ion batteries (LIBs). Recent research is focused on lithium-rich layered oxides (LLOs) which are solid solutions between Li_2MO_3 (where M = Ti, Mn and Ru) and $LiMO_2$ (where M = Cr, Mn, Fe, Co, Ni). LLOs have excess lithium in the TM layer in addition to lithium in lithium layer of rock salt derived structure. LLOs have gained attention because of their higher discharge capacity in the range of ~ 250 $mAhg^{-1}$. While most of the LLOs investigated so far contain 3d-TM ions (Mn, Fe, Co, Ni), recently there has been an interest in the study of the role of ruthenium in addition to 3d-TM ions. We have investigated ruthenium containing LLOs with a view to probe (i) the role of ruthenium and (ii) the concentration of excess lithium in the TM layers in producing higher discharge capacities. The results are discussed in the **Part 2** of the thesis.

In **Chapter 2.1**, we report synthesis, structure and the electrochemical behaviour of three new families of rock salt related LLOs of formula, $Li[Li_xM_{0.5-x/2}Ru_{0.5-x/2}]O_2$, $Li[Li_xM_{1-2x}Ru_x]O_2$ and $Li[Li_xM_{1-3x}Mn_xRu_x]O_2$ (M = Co and Ni). While $Li_9Co_{3.5}Ru_{3.5}O_{16}$ ($Li[Li_{0.125}Co_{0.4375}Ru_{0.4375}]O_2$), $Li_5Co_{1.5}Ru_{1.5}O_8$ ($Li[Li_{0.25}Co_{0.375}Ru_{0.375}]O_2$), $Li_5Co_2RuO_8$ ($Li[Li_{0.25}Co_{0.5}Ru_{0.25}]O_2$), Li_4CoRuO_6 ($Li[Li_{0.34}Co_{0.33}Ru_{0.33}]O_2$) and Li_4NiRuO_6 ($Li[Li_{0.34}Ni_{0.33}Ru_{0.33}]O_2$) compounds adopt the $LiCoO_2$ crystal structure, $Li_5Ni_2RuO_8$ ($Li[Li_{0.25}Ni_{0.5}Ru_{0.25}]O_2$), $Li_5CoMnRuO_8$ ($Li[Li_{0.25}Co_{0.25}Mn_{0.25}Ru_{0.25}]O_2$) and $Li_5NiMnRuO_8$($Li[Li_{0.25}Ni_{0.25}Mn_{0.25}Ru_{0.25}]O_2$) form in the Li_2RuO_3 crystal structure and $Li_9Ni_{3.5}Ru_{3.5}O_{16}$ ($Li[Li_{0.125}Ni_{0.4375}Ru_{0.4375}]O_2$) and $Li_5Ni_{1.5}Ru_{1.5}O_{85}O_8$ ($Li[Li_{0.25}Ni_{0.375}Ru_{0.375}]O_2$) crystallize in the Li_2TiO_3 structure. Electrochemical studies indicate that the Co-containing oxides exhibit a higher initial discharge capacity (for e.g. ~ 180 $mAhg^{-1}$ for Li_4CoRuO_6) as well as a higher reversible discharge capacity (~130 $mAhg^{-1}$ for Li_4CoRuO_6) compared to the corresponding Ni-analogs. Participation of oxide ions (higher oxidation state of Ru) in the redox process could explain the higher discharge capacity during the first cycle. Reduced capacity (capacity fade) during the subsequent cycles could arise from the oxygen evolution due to the redox process ($2O^{2-} \rightarrow 2O^{-} \rightarrow O_2$), which is not reversible. The present work shows that ruthenium incorporation in rock salt layered oxides along with Co/Ni appears to give a beneficial effect in producing a higher discharge capacity. In addition, the compounds crystallizing with the *R-3m* structure (related to $LiCoO_2$) appear to give a better reversible capacity than the compounds crystallizing in the *C2/c* structures (Li_2TiO_3 and Li_2RuO_3).